TABLE 2 — THERMAL BEHAVIOUR OF OXOPENTAFLUORONIOBATES

Compound	Decomp. temp. (°C)	Range of max. decomp. (°C)	Loss (%) observed at 500°	Theoretical loss (%) for the generation of Nb_2O_5 and $M^{II}O$
$[Cu(py)_4][NbOF_5]$	50	140-250	64·13	63·59
$[Ni(py)_4][NbOF_5]$	40	170-300	65·80	64·42
$[Zn(py)_4][NbOF_5]$	30	80-230	63·80	63·36
$[Cd(py)_4][NbOF_5]$	40	120-230	58·78	58·69
$[Co(py)_4][NbOF_5]$	40	150-240	63·21	64·13

the case of $[N(CH_3)_4][HNbOF_5]$ strong bands appeared at 930 and 955-965 cm^{-1}.

The compounds were studied thermogravimetrically as before[4] in the region 30-500° in a manually operated thermobalance. The thermal behaviour of $[M^{II}(py)_4]NbOF_5$ showed that loss of pyridine and fluorine took place simultaneously. The formation of $M^{II}NbOF_5$ also could not be observed. The residues obtained at 500° consisted of a mixture of Nb_2O_5 and metal oxide. The salient features of the thermal data are given in Table 2. The pyrolysis of $[N(CH_3)_4][HNbOF_5]$ was slow from 90° to 300°, thereafter the compound underwent very rapid decomposition and ultimately at 450° generated pure niobium pentoxide.

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Heteropoly-niobates, -tantalates & -vanadates

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Heteropolyniobates, -tantalates and -vanadates of the compositions $K_{10}H[VNb_{12}O_{38}.]20H_2O$, $K_8H_3[VTa_{12}O_{38}].26H_2O$ and $(NH_4)_2[MoV_6O_{19}].12H_2O$ have been prepared. Analytical data agree well with the proposed molecular formulae. Cell constants and space groups have been determined from X-ray studies.

REPORTS on heteropoly salts of niobium, tantalum and vanadium are very few[1-3]. The present note deals with the preparation and characterization of some new heteropoly salts, viz. potassium vanadoniobate, potassium vanadotantalate and ammonium molybdovanadate.

Aqueous solutions of freshly prepared[4] potassium hexaniobate, $K_7HNb_6O_{19}.13H_2O$, and potassium metavanadate were mixed in the molar ratio of 12:1 and refluxed for 4 hr. The resulting solution was kept under atmospheric conditions for three days and finally crystallization induced by keeping *in vacuo* when small needle-shaped crystals separated which were recrystallized thrice from hot water (Found: K, 15·32; V, 1·97; Nb, 44·27; H, 1·59. $K_{10}H[VNb_{12}O_{38}].20H_2O$ requires K, 15·44; V, 2·01; Nb, 44·15; H, 1·61%). The formations $K_{10}H[VNb_{12}O_{38}].20H_2O$ is in accord with that suggested by Lindqvist[5] for complex heteroanion of the type $[X^{n+}Nb_{12}O_{38}]^{(16-n)-}$.

The corresponding heteropoly tantalate has also been prepared as above starting from potassium vanadate and freshly prepared potassium hexatantalate[4]. Light yellow crystals of potassium vanadotantalate obtained, were crystallized from hot water (Found: K, 8·50; V, 1·35; Ta, 60·15, H, 1·49; $K_8H_3[VTa_{12}O_{38}].26H_2O$ requires K, 8·63; V, 1·41; Ta, 60·08; H, 1·52%). The formulation of the compound is in agreement with that suggested by Lindqvist[5] for heteroanion of the type $[X^{n+}Ta_{12}O_{38}]^{(16-n)-}$. Heteropoly molybdovanadate has been prepared similarly starting from ammonium metavanadate (0·2*M*) and molybdic acid (0·05*M*) solutions. Small fibrous, silky yellowish crystals of ammonium molybdovanadate obtained were crystallized from hot water (Found: N, 2·88; H, 3·29; Mo, 10·25; V, 31·50. $(NH_4)_2[MoV_6O_{19}].12H_2O$ requires N, 2·92; H, 3·34; Mo, 10·01; V, 31·92%). The formulation is in accord with that suggested by Keggin[6] for complex anion of the type $[V_6O_{19}]^{8-}$.

The results of the X-ray crystal diffraction studies of the compounds are given below:

(a) $K_{10}H[VNb_{12}O_{38}].20H_2O$: $a=15·66$, $b=26·10$, $c=8·40$ Å and $\alpha=\beta=\gamma=90°$. The system is orthorhombic. Volume per unit cell = 3433°29 Å^3. The space group is D_{2h}^2-P_{nnn}. Number of molecules per unit cell = 2. The observed density = 2·46 gl^{-1}.

(b) $K_8H_3[VTa_{12}O_{38}].26H_2O$: $a=16·56$, $b=35·12$, $c=14·72$ Å and $\alpha=\beta=\gamma=90°$. The system is orthorhombic. Volume per unit cell = 8560·96 Å^3. The space group is I_{41}/a. Number of molecules per unit cell = 4. The observed density = 2·79 gl^{-1}.

(c) $(NH_4)_2[MoV_6O_{19}].12H_2O$: $a=9·62\pm0·02$, $b=16·25\pm0·02$, $c=6·24\pm0·02$ Å, $\alpha=\beta=\gamma=90°$. The system is orthorhombic. Volume per unit cell = 975·46 Å^3. The space group is D_{2h}^2-P_{nnn}. Number of molecules per unit cell = 2. The observed density = 3·240 gcc^{-1} against the calculated density of 3·259 gcc^{-1}.

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